Controlled Undercooling of Liquid Iron in Contact with ZrO_2 and MgO Substrates under Varying Oxygen Partial Pressures

MARTIN E. VALDEZ, H. SHIBATA, and ALAN W. CRAMB

The objective of this study is to determine the conditions under which the inclusions present in liquid steel can act as heterogeneous nucleants for solidification. In order to study the factors that define the undercooling of a given metal/oxide couple, the undercooling of a pure iron sessile droplet in contact with Al_2O_3, ZrO_2, and MgO substrates was measured under controlled oxygen partial pressures by observing droplet recalescence. The results showed that the undercooling of iron, in contact with a particular substrate, did not have a unique value, but was significantly affected by the oxygen content on the gas phase. For oxygen partial pressures between 10^{-21} and 10^{-19}, the undercooling of iron on ZrO_2 substrates was stable and around 290 °C. In the same range of oxygen partial pressure, the undercooling of iron on MgO substrates remained below 100 °C due to the low stability of this oxide. At lower oxygen contents, substrate decomposition might be the cause for the observed drop in the undercooling of iron on ZrO_2 substrates to below 100 °C. The undercooling also decreased for increasing oxygen content as verified when the gas was changed from gettered $Ar/Ar-H_2$ to CO/CO_2 mixtures. The variation in undercooling was related to the wetting of the substrate by the liquid metal, where the deep undercooling observed in the ZrO_2 experiments occurred when the highest contact angle between the liquid metal and the substrate was achieved.

I. INTRODUCTION

THE objective of "oxide metallurgy"[1] applied to casting is to determine the conditions under which the inclusions present in liquid steel can act as heterogeneous nucleants for solidification. Solidification structure control through inoculation is a successful practice in aluminum production. However, in the oxide metallurgy approach, instead of using an external inoculation, *in-situ* precipitation of suitable inoculants is desired. The inclusions can be designed to favor heterogeneous nucleation in order to achieved a fully equiaxed structure[2,3] or to delay nucleation in order to take advantage of the high solidification rates expected during undercooled solidification. The design of a process in which the undercooling, and hence the solidification structure, can be controlled requires a deep understanding of the factors that define when and where nucleation occurs. This work is focused on the factors that determine the degree of undercooling necessary to solidify a metal when a specific surface is available for heterogeneous nucleation.

Original efforts on undercooling measurements concentrated on the measurement of the homogeneous nucleation undercooling.[4,5] This is an important parameter because it is the only undercooling that should be constant for a given metal. It is also the maximum undercooling measured for a metal, because any lower value of undercooling is related toheterogeneous nucleation on undesired solids and is discarded. In some experimental conditions the solids chemistry

and size can be controlled and the value of undercooling is referred to as the undercooling for heterogeneous nucleation.[6] Because solids are generally in equilibrium with elements dissolved in a metal at high temperatures, and because these elements (*e.g.,* oxygen and magnesium in equilibrium with magnesia) may affect the surface energies that define nucleation, the heterogeneous nucleation undercooling for a given solid/metal couple might not be constant.

In a previous work by Valdez *et al.,*[7] the effect of oxygen partial pressure on the undercooling of a pure iron sessile droplet in contact with an Al_2O_3 substrate was studied. The results are shown in Figure 1. The main observation was that the undercooling of liquid iron in contact with an Al_2O_3 substrate strongly depends on the oxygen partial pressure of the gas phase. With increasing PO_2 from 10^{-22} to 10^{-8} atm, the undercooling was observed to go through a maximum at 288 °C. The presence of a maximum in undercooling was verified in differential thermal analysis experiments using Al_2O_3 crucibles.[7] The undercooling decreased for low oxygen partial pressures (probably due to increasing aluminum dissolved in the droplet from substrate decomposition) and for high oxygen partial pressure (due to the effect of increasing oxygen content in the liquid iron on the surface tension of liquid iron). The contact angle of the sessile droplets used to measure the undercooling shown in Figure 1 also went through a maximum.

The conclusion from our previous work[7] was that deep undercoolings are possible for low oxygen contents, provided there is no substantial decomposition of the substrate. The hypothesis for this article is that the effect of oxygen partial pressure in the heterogeneous nucleation undercooling should vary with different substrates. The experimental approach was to measure the undercooling of a pure iron sessile droplet in contact with ZrO_2 and MgO substrates under controlled oxygen partial pressures by observing droplet recalescence. As discussed subsequently, the difference between the substrates investigated is that, at 1600 °C, ZrO_2 is as stable or more stable than Al_2O_3, while MgO is clearly less stable.

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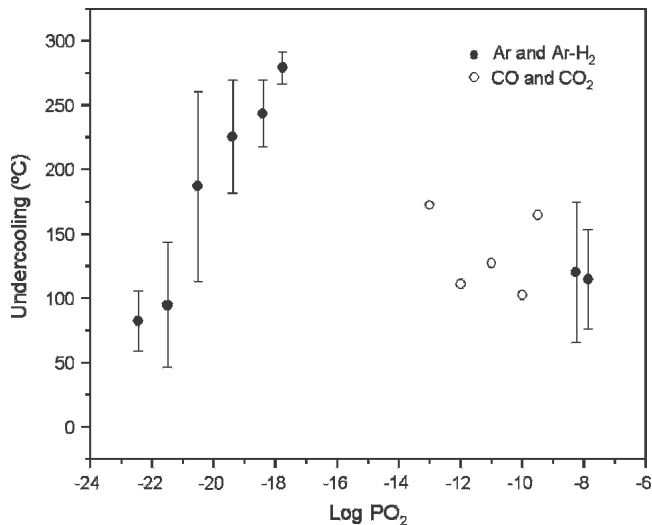
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Fig. 1—Undercooling for Fe/Al_2O_3 as a function of PO_2 (Valdez *et al.*[7]).

II. EXPERIMENTAL

The experimental approach of this work consisted of measuring the undercooling of a pure iron droplet on top of oxide substrates, using a sessile drop setup. The sessile drop technique is usually used to measure the contact angle of liquid metals in contact with substrates and the surface tension of liquid metals. The undercooling was measured by slowly cooling the droplet/substrate system and by detecting solidification during the increase in brightness of the droplet when the latent heat was released (Figure 2).

The detailed experimental apparatus and the oxygen control setup have been discussed in a previous work.[7] Figure 3 shows a schematic of the experimental apparatus.

The samples were melted and solidified inside a tube furnace. Because the oxygen content is known to affect the contact angle and surface tension of liquid metals[8–16] and, because a strong relation between wetting, undercooling, and oxygen partial pressure was already observed in previous work,[7] a test chamber with a controlled/inert environment was used. Different gases were flown inside the furnace with the objective of purging the system and controlling the oxygen partial pressure. The flow rate was set up between 100 and 200 mL/min, and a time period of approximately 5 hours was necessary to purge the entire system from any trace of air. "Downstream" from the furnace, the gas was flown through a solid-stabilized-zirconia oxygen sensor that continuously monitored the oxygen partial pressure in the gas (PO_2). The range of PO_2 that was achieved with different experimental conditions (Ar-5 pct H_2, Ar, or CO-CO_2 mixtures) was from 10^{-23} atm to the limit established by the oxidation of iron. The details of the range achieved with each gas type as well as the calibration of the oxygen measurements were published previously.[7]

The sample was heated at 3 °C/min to the soaking temperature (1600 °C) and left at this temperature for 1 hour before cooling. The cooling rate was also 3 °C/min. The recording of the video started at the same time as the cooling. Further analysis of the video allowed the determination of the contact angle of the system at 1600 °C as well as the degree of undercooling necessary for solidification.
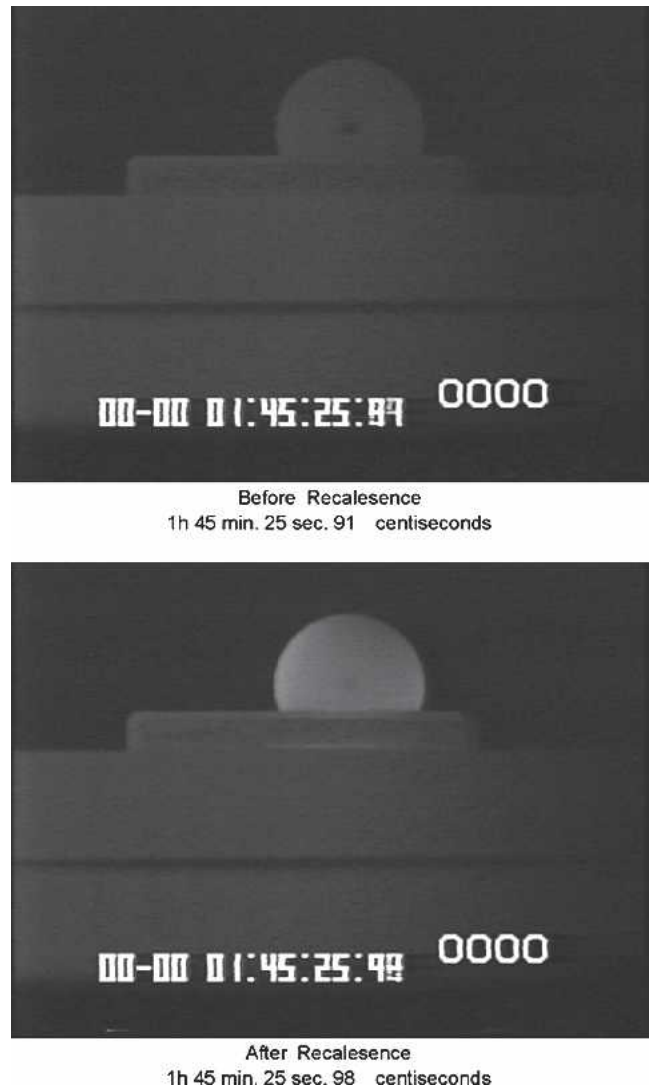

Before Recalesence
1h 45 min. 25 sec. 91 centiseconds

After Recalesence
1h 45 min. 25 sec. 98 centiseconds

Fig. 2—Photograph of the droplet before and after recalescense showing that the start of solidification is detected as a sudden change in brightness.

The metal samples were pure iron (purity 99.995 pct) of approximately 0.25 g. The substrates are described in Table I. The properties of the Al_2O_3 substrates correspond to those used for the results presented in Figure 1. TiO_2 is also included in the table even though the substrate became unstable and transformed to Ti_3O_5 during the experiments. No further results on the use of TiO_2 substrates will be presented.

III. EXPERIMENTAL RESULTS

A. *Pure Iron on ZrO_2*

This section describes the results of the experiments performed using pure iron on top of ZrO_2 single crystals of (100) orientation. A total of 17 recalescense experiments were done using Ar-H_2 and Ar gas, moving from low to high oxygen partial pressures in two series of experiments. The change in undercooling and contact angle is shown in Figures 4 and 5. The behavior was similar to that reported before for Al_2O_3[7] (Figure 1). First, there was an increase
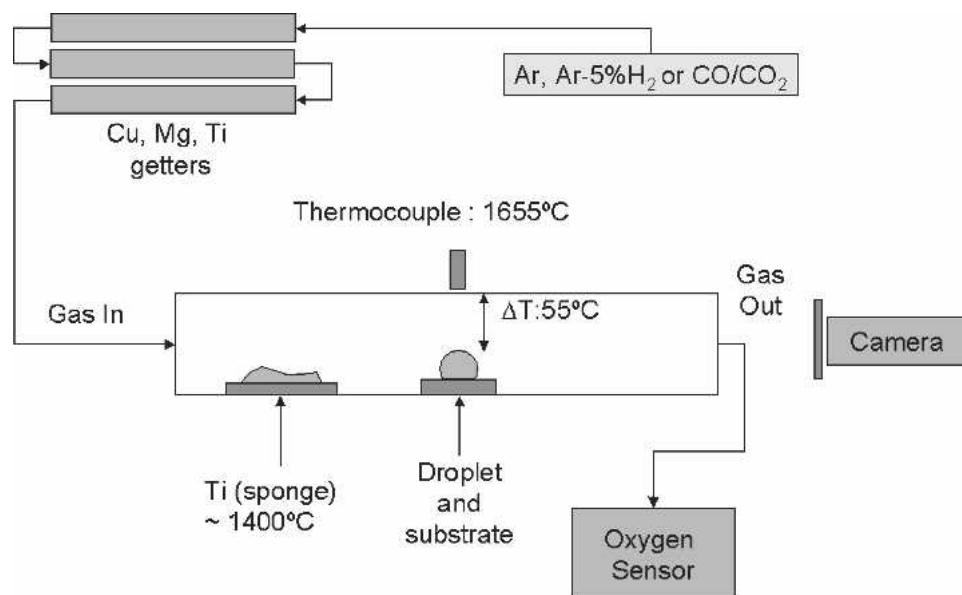
Fig. 3—Experimental apparatus showing the system to clean the gas upstream and an oxygen sensor downstream.

Table I. Substrates

Material	Company	Orientation	Roughness (Rt(nm))*	Thickness
Al_2O_3	Vesuvius	polycrystalline	7.3	2.4 mm
Al_2O_3	Alfa-Aesar	A Plane	—	1 mm
MgO	Crystal	111	1.42	—
TiO_2	Crystal	100	0.59	0.5 mm
ZrO_2	Crystal	100	1.11	—

*Rt: represents the distance from the highest peak over the entire assessment length to the lowest valley over the entire assessment length.

Fig. 4—Change of undercooling of pure iron on top of ZrO_2 (100) substrate as a function of PO_2—individual measurements.

on undercooling with increasing PO_2 from 0 °C to a maximum of 289 °C, the undercooling remaining high in a range of PO_2 between $10^{-21.5}$ to 10^{-19} atm. Finally, as the PO_2 measured in the downstream oxygen sensor increased above 10^{-19} atm, a drop in the undercooling was observed. The decrease in undercooling matched an increase in the wetting of the substrate, as reported for Al_2O_3.[7]

The small arrows in Figures 4 and 5, next to the measurements done under $PO_2 > 10^{-19}$ atm, are an indication that the real PO_2 in contact with the droplet may be higher. The measured value of PO_2 is caused by the buffering effect of the Ti that does not allow the downstream oxygen to increase. This was verified by measuring the oxygen partial pressure in both a "downstream" and an "upstream" position. For PO_2 below an approximate value of $10^{-19}/10^{-18}$ atm, the upstream PO_2 is a little lower than the downstream PO_2 due to leakages. When the incoming PO_2 is increased above $10^{-19}/10^{-18}$ atm, the PO_2 downstream does not change, provided there is enough Ti sponge surface available inside the main furnace (Figure 3). The actual oxygen content in equilibrium with the droplet under these conditions can be estimated from the already reported values of contact angle of Fe on ZrO_2.[17,14] For example, Nakashima[17] measured a contact angle of 90 deg for experiments on a pure iron/ZrO_2 substrate under Ar gas at 1600 °C
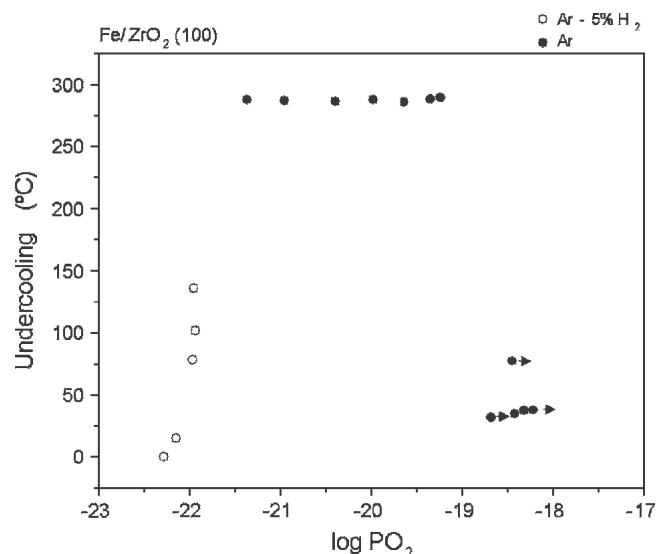
and 110 to 120 deg for experiments in H_2. According to his article, the drop in contact angle as the oxygen content increases can be attributed to an oxygen partial pressure close to 10^{-10} atm. Further evidence that the samples with low undercooling and contact angles were in equilibrium with a PO_2 higher than the one measured in the downstream sensor is derived from the thermodynamic estimations of the PO_2 for the formation of iron oxide compounds. Fe-O-Zr compounds were found in the interface between the droplet and the substrate for experiments in the high PO_2 range, as shown in the scanning electron microscopy (SEM) pictures and the line-scan energy dispersive X-ray analyzer (EDX) in Figure 6. The formation of Fe-Zr-O solutions is only possible for $PO_2 > 10^{-9}$ atm.[20,18]

Due to the uncertainty in the actual oxygen in equilibrium with the sample for the measurements done with gettered Ar for PO_2 above $10^{-19}/10^{-18}$ atm, the intermediate range of PO_2 (between 10^{-19} and 10^{-10}) was covered with CO-CO_2 experiments. Four different oxygen partial pressures were set up by changing the relative amounts of CO and CO_2.

The effect of oxygen partial pressure on undercooling for Fe/ZrO_2 can then be replotted as a function of oxygen partial pressure, including the Ar and Ar-H_2 undercoolings measured in the low PO_2 range ($PO_2 < 10^{-19}$ atm in Figure 4), the CO-CO_2 experiments for intermediate oxygen partial pressure, and the points that showed low contact angle and undercoolings in Figures 4 and 5 (points with arrows)
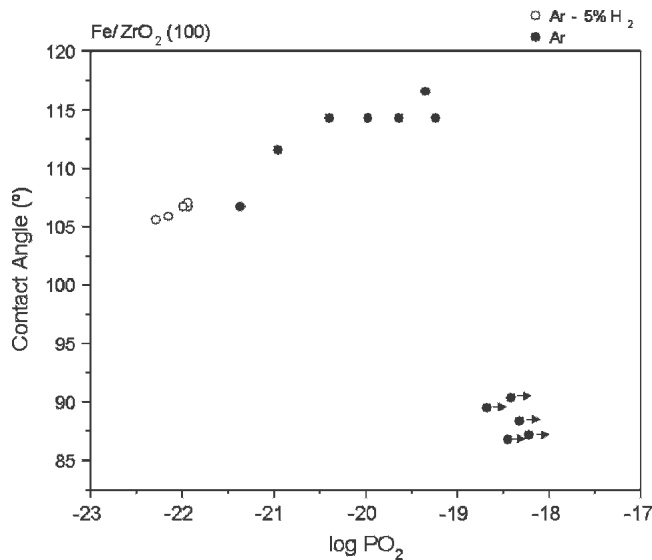

Fig. 5—Change of contact angle of pure iron on top of ZrO_2 (100) substrate as a function of PO_2—individual measurements.

moved to $PO_2 > 10^{-10}$ atm. The results are shown in Figure 7. The error bars in the CO-CO_2 results are caused by two factors. The uncertainty in undercooling is caused by changes in the melting temperature due to incorporation of carbon in the sample, and the uncertainty in the PO_2 is due to the changes in the oxygen in equilibrium with a given CO/CO_2 ratio when the temperature decreases from 1600 °C to the solidification temperature.

Even though the overall behavior is similar to the one observed for the experiments performed on alumina substrates, the range of PO_2 in which the undercooling is high is larger in the ZrO_2 experiments. The undercooling seems also to be more stable (constant) that in the case of Al_2O_3. In the case of alumina, the undercooling drops to both sides of a peak rather than achieving a plateau as observed for ZrO_2.

B. Pure Iron on MgO

The measurement of undercooling of pure iron on magnesia was performed using MgO single crystals of orientations (111) and (100). Contamination of the sample with SiO_2 from the Al_2O_3 polycrystalline disk and the semitube that supports the substrate (Al_2O_3 99.82 pct and SiO_2 0.06 pct) was observed. In order to minimize this contamination, an Al_2O_3 single crystal (higher purity) was placed between the MgO substrate and the polycrystalline Al_2O_3. The range of PO_2 for the experiments with MgO was limited to 10^{-22} to 10^{-18} atm due to the impossibility of controlling the PO_2 in gettered Ar for higher oxygen partial pressures (as discussed previously); the intermediate range of PO_2 (between 10^{-18} and 10^{-10}) was covered with CO-CO_2 experiments. The results are shown in Figure 8, including some experiments performed in MgO (100) single crystals.[19] The maximum undercooling was around 170 °C and the minimum was 20 °C.

The contact angle observed for the experiments in MgO substrates contains errors due to the difficulties in determining
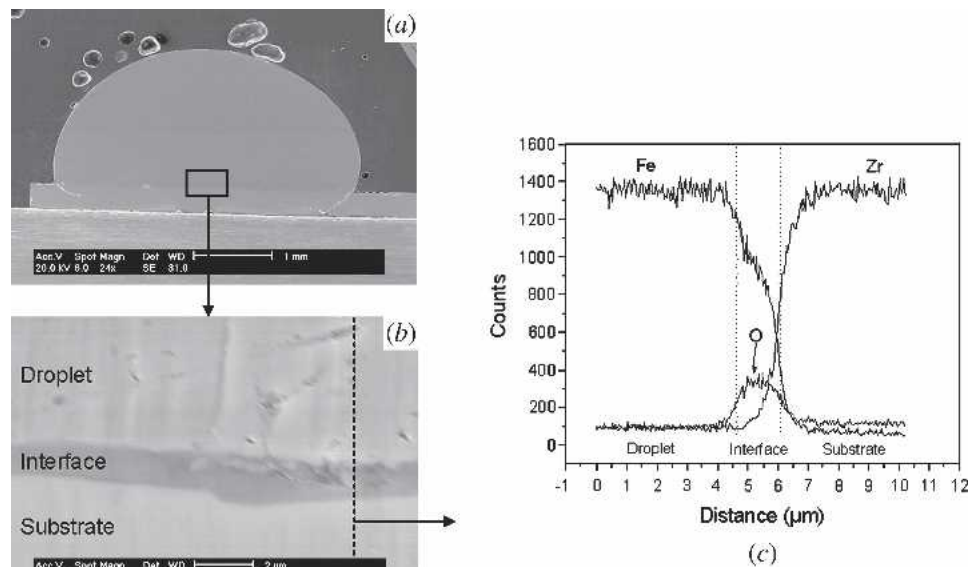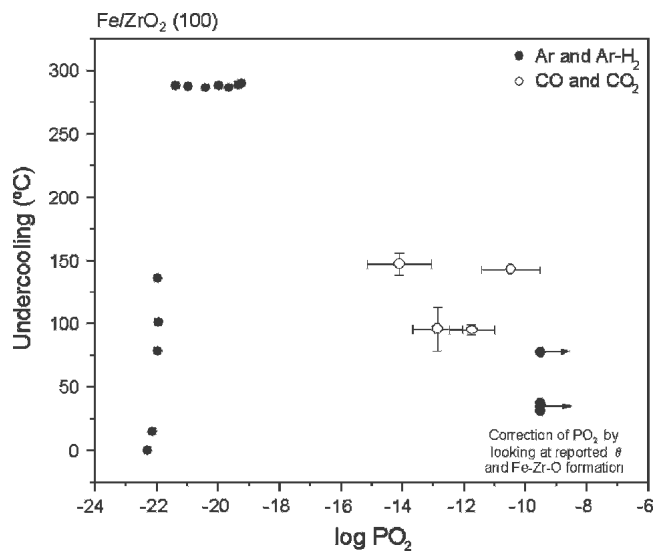

Fig. 6—Analysis of the interface between droplet and ZrO_2 substrate after high PO_2 experiments: (a) general view of the droplet, (b) detail of the interface layer between the droplet and the substrate, and (c) change in composition with distance from top to bottom trough the dotted line in (b).

Fig. 7—Undercooling of Fe on ZrO_2 for Ar and Ar-H_2 experiments ($PO_2 < 10^{-19}$), CO/CO_2 mixtures, and the Ar experiments with $PO_2 > 10^{-19}$ corrected by contact angle and Fe-Zr-O formation.
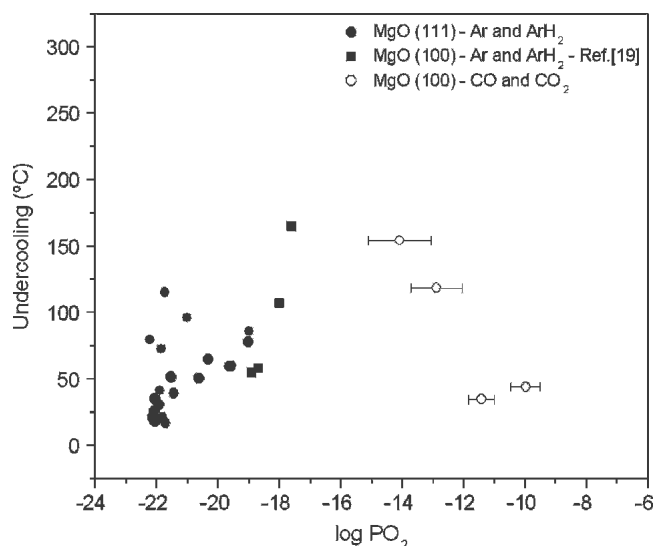

Fig. 8—Change of undercooling of pure iron on top of MgO (111) and (100) substrate as a function of PO_2—individual measurements.

Fig. 9—Comparison between the first and last experiments showing the decrease in the thickness of the MgO substrate.

the base line. This was a consequence of substrate evaporation that caused the droplet to have a nonuniform shape (Figure 9). The contact angle measured under these conditions did not show any particular trend with oxygen content and was in the range of 90 to 115 deg. Shibata[19] measured around 70 deg for pure iron on MgO (100) under purified Ar (10^{-18} to 10^{-17} atm). The values collected from the *Slag Atlas*[20] for pure iron on MgO at 1600 °C in Ar and H_2 are in the range 96 to 127 deg, and the values published by Ogino[21] are in the range 95 to 110 deg.

The undercoolings of iron on MgO are similar to the values shown in Figures 1 and 6 for the low range of PO_2 ($<10^{-21}$ atm for ZrO_2 and $<10^{-20}$ atm for Al_2O_3) and for the range covered by CO/CO_2. However, in the case of
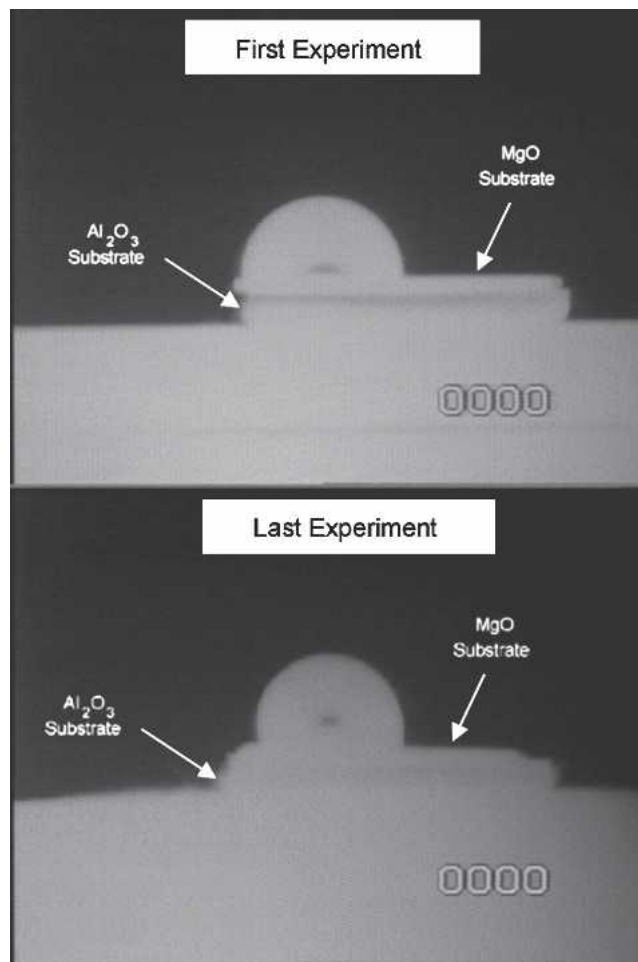
MgO, the undercooling remains low in the range of oxygen partial pressures where Al_2O_3 and ZrO_2 showed deep undercooling (between 10^{-21} and 10^{-18} atm). The main difference between MgO and Al_2O_3 or ZrO_2 is that, for temperatures above the boiling point of magnesium ($\sim$1100 °C), MgO is less stable. The decomposition of the MgO substrate was verified by SEM/EDX and by direct observation during the experiments (Figure 9). The MgO substrate thickness decreased by reaction with the Al_2O_3 substrate placed below and through vaporization. Right under the metal droplet, the thickness decreased from the original 500 μm to 415 μm. Away from the droplet, the reaction with MgO was verified due to the formation of spinel with the Al_2O_3 substrate placed below and vaporization (the thickness decreased from 500 to 300 μm). Besides, a thin film of $MgAl_2O_4$ covered the Al_2O_3 polycrystalline substrate as far as 1.6 cm from the droplet. The silica contamination was not totally avoided but was significantly reduced with respect to the experiments without the extra Al_2O_3 single crystal. The SEM/EDX showed some small patches with higher Si content, but there were no silicon traces in the droplet/substrate interface. As expected, there was no reaction product between the Fe droplet and the MgO substrate in this range of oxygen partial pressure.

IV. DISCUSSION

The results of this article confirm that the substrate can influence the undercooling in several ways. The most obvious effect is due to the fact that the surface at which heterogeneous nucleation occurs is different. Besides, if the substrate becomes unstable and substantial decomposition of the substrate occurs, the interaction between the oxide and the metal is modified. The modification of the properties of the oxide/metal interface and the associated changes in the chemical composition of the liquid, affects the undercooling.

In order to understand the behavior of different substrates, the relative stability of the oxides should be compared. The decomposition of the substrate into the dissolved elements in the liquid metal and in equilibrium with both the gas phase and the oxide is the expected condition for the sessile drop experiment. Because decomposition of the substrate into its elements dissolved in the liquid metal should occur at any oxygen partial pressure, this reaction is not useful when comparing the stability of different substrates. However, it is interesting to analyze a generic reaction of decomposition of an oxide (M_xO_{2y}) without dissolution in the metal according to Eq. [1].

$$M_xO_{2y}\,(s) \longrightarrow x\,M\,(l) + y\,O_2\,(g) \qquad [1]$$

$$K = \frac{aM^x \cdot PO_2^y}{aM_xO_{2y}} = PO_2^y \qquad [2]$$

The PO_2 calculated with Eq. [2] is the oxygen partial pressure in the gas phase under which decomposition according to Reaction [1] will occur (PO_2^D). The calculation of PO_2^D by this means is independent of the presence of the droplet and an exclusive property of the substrate and the temperature. Table II shows the PO_2^D for the different oxides studied in this work at 1600 °C. The free energies of the different reactions are from well-known sources.[18,22] Because Mg is a vapor at 1600 °C, a partial pressure of Mg equal to 1 atm was used for the calculation.

At PO_2 below the PO_2^D, the substrate should be able to decompose into its components. The decomposition oxygen partial pressure (PO_2^D) for MgO is high, and hence, the range of PO_2 in which the substrate is not stable is larger. In the case of Al_2O_3 and ZrO_2, decomposition should occur at decreasing oxygen partial pressures. Figure 10 is a schematic of the undercooling of pure iron on ZrO_2, Al_2O_3, and MgO as a function of PO_2. The figure shows that the PO_2^D matches the minimum PO_2 in which deep undercoolings were observed. This agrees with the fact that the experiments performed on MgO single crystals showed low values of undercoolings for the range of PO_2 between 10^{-22} and 10^{-18}. The maximum undercooling for magnesia could be located for PO_2 higher than PO_2^D for MgO. If it is considered that increasing oxygen contents also produces a drop in the undercooling, as verified by the CO/CO_2 experiments, it is probable that deep undercoolings are not possible for a droplet in contact with a MgO surface. At this point, it is possible to conclude that even though the undercooling of a given metal/oxide couple is affected by the oxygen partial pressure, for some nonstable oxides such as MgO, the variation may be

minimum, while for some stable oxides, the complete range of undercoolings from 0 °C to 290 °C are possible.

There are other interesting results, first among them being the fact that the maximum undercooling observed in the ZrO_2 experiments is followed by a decrease in wettability (Figures 4 and 5). In a previous article,[7] the relation between wettability and undercooling was discussed, and it was hypothesized that, for the undercooling to increase as wettability decreases, the nucleation has to be affected by the degree of interaction between the metal and the substrate. In this way, as wettability decreases, the liquid could become "less aware" of the presence of the substrate and the nucleation would move from heterogeneous nucleation to homogeneous nucleation. Under these conditions, the maximum undercooling should be close to homogeneous nucleation, independent of the substrate composition but dependent on the metal composition. These observations match ours, given the fact that the value of the maximum undercooling observed for the Al_2O_3 and ZrO_2 experiments was the same, and in extremely close agreement with Turnbull results.[4] The comparison of the maximum undercooling for each oxide is shown in Table III. The table also

Table II. Oxygen Partial Pressure for Decomposition of Different Substrates (Log PO_2^D)

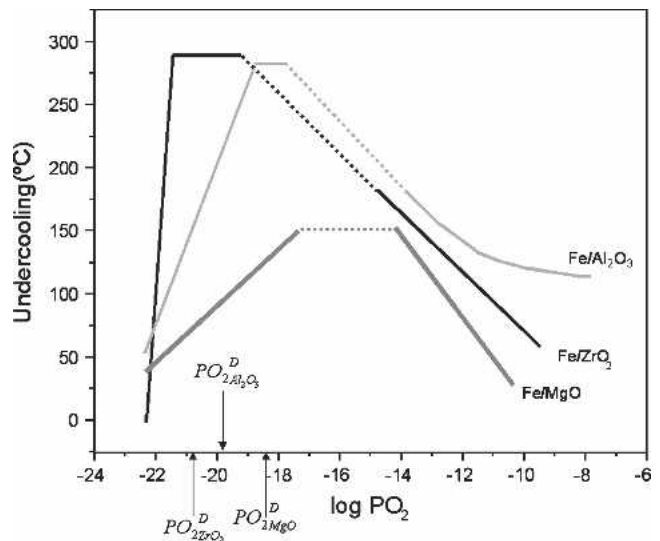| Substrate	Log PO_2^D
ZrO_2	−20.86
Al_2O_3	−19.95
MgO	−18.48

Fig. 10—Schematic of the undercooling of pure iron on ZrO_2, Al_2O_3, and MgO as a function of PO_2.

Table III. Maximum Undercooling Measured for Fe

		Valdez et al.[7]		
	Turnbull	Al_2O_3[7]	ZrO_2	Quartz
Fe	295	288	289	285.6

includes the values measured for Fe on quartz (PO$_2$:$10^{-18.3}$) in which the maximum undercooling was 285.6 °C.

Turnbull[4] measured the undercooling of Fe among other metals under helium atmosphere. The conditions under which Turnbull experiments were performed were designed to avoid heterogeneous nucleation. The droplets were placed on top of a quartz flake or inside a flux to avoid heterogeneous nucleation. Turnbull measured a wide distribution of solidification temperatures and reported the most significant undercooling as being characteristic of the metal. It is interesting that, in the experiments presented in this work, the value of undercooling under a condition where a heterogeneous nucleation surface was clearly available was the same as the maximum undercooling reported by Turnbull for homogeneous nucleation. It seems that, under the conditions where a maximum is achieved, the system solidifies close to a homogeneous undercooling value. It can be concluded that the maximum undercooling is a function of the type of metal but not of the type of substrate. This is true provided a maximum is achieved, because, in the case of the MgO experiments, the undercooling remained below 175 °C.

V. CONCLUSIONS

In order to study the factors that define the undercooling of a given metal/oxide couple, the undercooling of a pure iron droplet in contact with ZrO$_2$ and MgO substrates was measured under controlled oxygen partial pressures in a sessile drop experiment. The results were compared with experiments performed by the same authors on Al$_2$O$_3$ substrates.

The experimental results show that the undercooling of iron is not unique but is affected by the oxygen content. For intermediate oxygen partial pressures, the undercooling of iron on Al$_2$O$_3$ and ZrO$_2$ substrates was around 290 °C but remained below 150 °C for the less stable MgO. At low oxygen contents, substrate decomposition might be the cause for the observed drop in the undercooling of iron in Al$_2$O$_3$ and ZrO$_2$ substrates to below 100 °C. The minimum oxygen partial pressure under which deep undercoolings were measured is similar to the oxygen partial pressure for substrate decomposition. The undercooling also decreased for increasing oxygen content as verified when the gas was changed from gettered Ar/Ar-H$_2$ to CO/CO$_2$ mixtures.

Besides, it was observed that the maximum undercooling is the same for different stable substrates (such as Al$_2$O$_3$ and ZrO$_2$), that the undercooling increases as the wettability decreases, and that the maximum undercooling was similar to the values reported previously as homogeneous nucleation undercooling. All of these observations suggest that for the conditions achieved in this article, homogeneous nucleation of the metal is possible even when a

heterogeneous nucleation surface is clearly available. Because the homogeneous undercooling is a property of the metal and not of the substrate, the maximum undercooling should be different for other metals. The undercooling of different metals will be discussed in future works.

REFERENCES

1. J. Takamura and S. Mizoguchi: *Proc. 6th Int. Iron Steel Congr.*, ISIJ, ed., Nagoya, 1990, pp. 21-26 and pp. 591-604.
2. J. Kim: Master's Thesis, Carnegie Mellon University, Pittsburgh, PA, 2005.
3. H. Fujimura, S. Tsuege, Y. Komizo, and T. Nishizawa: *Tetsu-to-Hagané*, 2001, vol. 87 (11), pp. 29-34.
4. D. Turnbull and R.E. Cech: *J. Appl. Phys.*, 1950, vol. 21, pp. 804-10.
5. H. Biloni and W. Boettinger: *Physical Metallurgy*, 4th ed., Elsevier Science, New York, NY, 1996, pp. 669-842.
6. K. Nakajima, H. Hasegawa, S. Khumkoa, and S. Mizoguchi: *Metall. Mater. Trans. B*, 2003, vol. 34B, pp. 539-47.
7. M. Valdez, P. Uranga, K. Fuchigami, H. Shibata, and A.W. Cramb: *Metall. Mater. Trans. B,* 2006, vol. 36B, in press.
8. S. Ueda, H. Shi, X. Jiang, H. Shibata, and A.W. Cramb: *Metall. Mater. Trans. B*, 2003, vol. 34B, pp. 503-08.
9. K. Ogino, K. Nogi, and Y. Koshida: *Tetsu-to-Hagané*, 1973, vol. 59 (10), pp. 1380-87.
10. K. Ogino, A. Adachi, and K. Nogi: *Tetsu-to-Hagané*, 1973, vol. 59 (9), pp. 1237-44.
11. N. Takiuchi, T. Taniguchi, N. Shinozaki, and K. Mukai: *J. Jpn. Inst. Met.*, 1991, vol. 55 (1), pp. 44-49.
12. Z. Jun and K. Mukai: *Iron Steel Inst. Jpn. Int.*, 1998, vol. 38 (10), pp. 1039-44.
13. B.T. Eldred and P.D. Ownby: *Trans. JWRI*, 2001, vol. 30, pp. 69-74.
14. N. Shinozaki, T. Fujita, and K. Mukai: *Metall. Mater. Trans. B*, 2002, vol. 33B, pp. 506-09.
15. Z. Yuan, K. Mukai, K. Takagi, and M. Ohtaka: *J. Jpn. Inst. Met.*, 2001, vol. 65 (1), pp. 21-28.
16. A.T. Hasouna, K. Nogi, and K. Ogino: *Trans. Jpn. Inst. Met.*, 1998, vol. 29 (9), pp. 748-55.
17. K. Nakashima, K. Takihira, T. Miyazaki, and K. Mori: *J. Am. Ceram. Soc.*, 1993, vol. 76 (12), pp. 3000-08.
18. Richard Fruehan: *The Shaping and Treating of Steel*, 11th ed., The AISE Steel Foundation, Warrendale, PA, 1998.
19. H. Shibata, X. Juang, M. Valdez, and A. Cramb: *Metall. Trans. B*, 2004, vol. 35B, pp. 179-81.
20. K.C. Mills: *Slag Atlas, 2nd ed.,* Verlag Stahleisen GmbH, Düsseldorf, Germany, 1995.
21. K. Ogino, A. Adachi, and K. Nogi: *Tetsu-to-Hagané*, 1973, vol. 59 (9), pp. 1237-44.
22. D.R. Gaskell: *Introduction to the Thermodynamics of Materials*, 3rd ed., Taylor & Francis, New York, NY, 1995.